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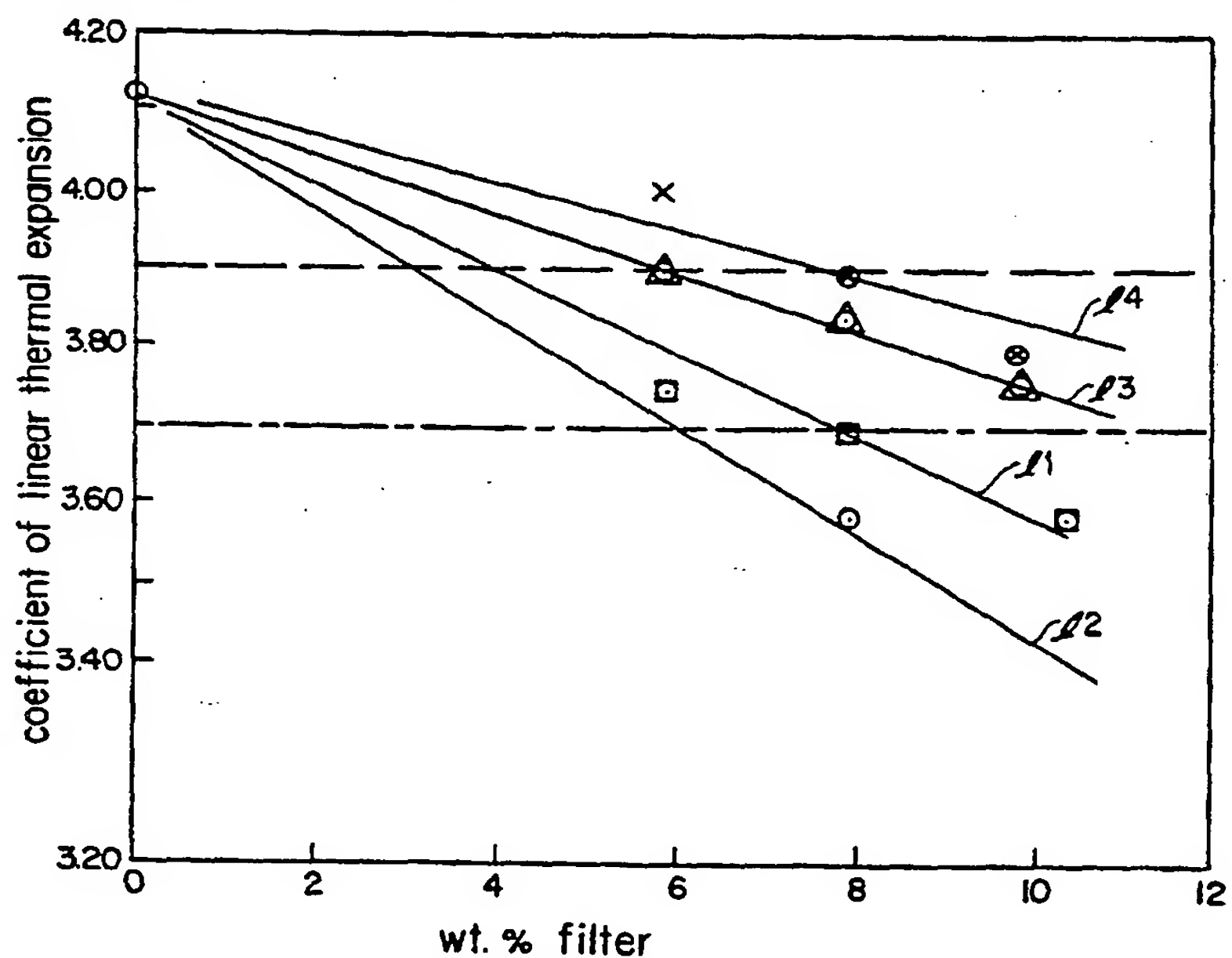
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(54) Filled polymeric blend.

(57) Filled polymer blends comprising a polycarbonate, a rubber modified copolymer of a vinyl aromatic monomer and from 4 to 18 weight percent of an inorganic filler.

FIG. 1



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FILLED POLYMERIC BLEND

The present invention relates to novel polymeric molding compositions comprising an amorphous polymer matrix and an inorganic filler. More particularly the present invention relates to such a polymeric blend having improved properties, particularly reduced coefficient of linear thermal expansion (CLTE), a high dart impact resistance, and good resistance to the effects of heat. The above composition is particularly useful in the preparation of molded objects particularly parts having large surfaces prepared by injection molding techniques, having reduced notch sensitivity in impact resistance and having predictable finished dimensions and smooth finish. Such properties are particularly desired for exterior automotive body panels.

U.S. Patent No. 4,098,734 discloses blends comprising a matrix interpolmer, a grafted rubber copolymer, a polymer other than the two foregoing polymers having a solubility parameter in the range of 8.5 to 13 and an inorganic filler. Examples of such blends comprising an ABS resin, about 14 percent of a clay, and polymethylmethacrylate or cellulose butyrate were disclosed. The reference further taught that polycarbonate could also be employed in the blend.

In Japanese Patent No. 52/63954 there are disclosed blends composed of 20 to 45 weight percent of an ABS resin, 45 to 20 weight percent of a polycarbonate resin and from 5 to 30 weight percent talc. Such compositions have been found to lack suitable heat distortion properties and also to be deficient in toughness as measured for example by Dart impact resistance or notched Izod impact values.

In certain applications such as exterior automotive injection molded parts it is desirable to provide low temperature impact resistance as well as reduced coefficient of linear thermal expansion and high temperature distortion resistance all in one polymeric resin. Unless the coefficient of linear thermal expansion (as measured according to ASTM D696) is less than $7.0 \times 10^{-5}/^{\circ}\text{C}$ ($3.9 \times 10^{-5}/^{\circ}\text{F}$) over the temperature range of 21 to 49 $^{\circ}\text{C}$ (70 to 120 $^{\circ}\text{F}$) extremes in temperature conditions can result in misfitting of various components of the finished assembly. A door or fender component which expands excessively will in extreme heat conditions result in buckling or misfit in the assembled finished product. Equally important is impact resistance as measured by dart impact resistance, particularly at low temperatures when thermoplastic resins are particularly subject to cracking under impact. Generally improved coefficients of linear thermal expansion can be obtained by the incorporation of increased amount of fillers, however, impact resistance, particularly low temperature impact resistance, is often reduced to unacceptable levels. Fibrous reinforcing additives such as fiber glass are very efficient in lowering the CLTE, however, such fibers typically are visible in the surface of the resulting object thereby producing unacceptable surface properties.

Accordingly it would be desirable if there were provided an improved polymeric blend having both a reduced coefficient of linear thermal expansion while retaining acceptably high dart impact resistance, particularly low temperature dart impact resistance and less notch sensitivity.

In addition it would be desirable if there were provided such an improved polymeric blend that additionally retains a high heat distortion under load such that parts prepared therefrom may be exposed to elevated temperatures without distortion.

Figure 1 shows the relationship between CLTE and amount of added filler for 4 selected fillers further defined in Experiment 4.

Figure 2 shows the relationship between dart impact strength and amount of added filler for 4 selected fillers further defined in Experiment 4.

According to the present invention there is now provided a filled polymeric blend comprising:

- (A) from 40 to 80, preferably 50 to 80 percent by weight of an aromatic polycarbonate;
- (B) from 5 to 50, preferably from 5 to 46 percent by weight of a rubber modified homopolymer or copolymer of a vinyl aromatic monomer;
- (C) from 4 to 18 weight percent of an inorganic filler selected such that (i) at least 98 weight percent of the filler particles in the final blend have a particle diameter (large dimension) less than 44 micrometers (μm) and (ii) the average filler particle diameter to thickness (large dimension to small dimension) ratio is from 4 to 24.

said blend having a coefficient of linear thermal expansion (CLTE) of $7.0 \times 10^{-5}/^{\circ}\text{C}$ ($3.9 \times 10^{-5}/^{\circ}\text{F}$) or less, a dart impact at -29 $^{\circ}\text{C}$ (-20 $^{\circ}\text{F}$) of at least 11.3 joules (100 in lbs); and a heat distortion temperature under load (DTUL) per ASTM D-648-82 at 455 kPa (66 psi) of at least 110 $^{\circ}\text{C}$ (230 $^{\circ}\text{F}$).

In measuring CLTE the technique employed is that of ASTM D696. Dart impact strength is instrumented dart impact strength measured according to ASTM D3763-86, with a 2.2 meter per second (5 mile/hour) velocity and a 1.3 centimeter (0.5 inch) diameter dart.

The aromatic polycarbonate resins usefully employed according to the present invention are those previously known and described in the prior art. More particularly such resins include the polycarbonate resins obtained by the interfacial polymerization or solution polymerization of a dihydroxyaryl compound, especially a bisdihydroxyaryllalkane, with phosgene or a bischloroformate in the presence of methylene chloride and an acid binding agent such as an alkali metal hydroxide or pyridine. Especially well suited aromatic polycarbonates include bisphenol A polycarbonate, tetrabromobisphenol A polycarbonate, tetramethyl- bisphenol A polycarbonate, 1,1-bis(4-hydroxyphenyl)-1-phenylethane polycarbonate and mixtures thereof.

Rubber modified homopolymers and copolymers of vinyl aromatic monomers include the rubber modified homopolymers and copolymers of styrene or α -methylstyrene with a copolymerizable comonomer. Preferred comonomers include acrylonitrile which may be employed alone or in combination with other comonomers particularly methylmethacrylate, methacrylonitrile, fumaronitrile and/or an N-arylmaleimide such as N-phenylmaleimide. Preferred copolymers contain from 70 to 90, more preferably from 70 to 80 percent styrene monomer and 30 to 10, more preferably 30 to 20 percent acrylonitrile monomer.

Suitable rubbers include the well known homopolymers and copolymers of conjugated dienes, particularly butadiene; as well as other rubbery polymers such as olefin polymers, particularly copolymers of ethylene, propylene and optionally a nonconjugated diene, or acrylate rubbers, particularly homopolymers and copolymers of alkyl acrylates having from 4 to 6 carbons in the alkyl group. In addition, mixtures of the foregoing rubbery polymers may be employed if desired. Preferred rubbers are homopolymers of butadiene and copolymers thereof with up to about 30 percent by weight styrene. Such copolymers may be random or block copolymers and in addition may be hydrogenated to remove residual unsaturation.

The rubber modified copolymers are preferably prepared by a graft generating process such as by a bulk or solution polymerization or an emulsion polymerization of the copolymer in the presence of the rubbery polymer. In the emulsion polymerization to form graft copolymers of rubbery substrates it is previously known in the art to employ agglomeration technology to prepare large and small rubber particles containing the copolymer grafted thereto. In the process various amounts of an ungrafted matrix of the copolymer are also formed. In the solution or bulk polymerization of a rubber modified copolymer of a vinyl aromatic monomer, a matrix copolymer is formed. The matrix further contains rubber particles having copolymer grafted thereto and occluded therein.

A particularly desirable product comprises a rubber modified copolymer blend comprising both the mass or solution polymerized rubber modified copolymer and additional quantities of an emulsion polymerized and preferably agglomerated rubber modified copolymer containing a bimodal particle-sized distribution. A most preferred rubber modified copolymer comprises a butadiene rubber modified copolymer. Butadiene rubber modified copolymers of styrene and acrylonitrile are referred to in the art as ABS resins.

To obtain a resulting polymeric blend meeting the requirements of the present invention it is desirable to employ specific concentrations of suitable fillers having elongated structures. It has now been discovered that spherical shaped fillers lack ability to lower the CLTE of resulting polymer blends compared to elongated fillers. The measurement of the filler large dimension/small dimension (diameter/thickness) ratio can best be done by first preparing a thin section by freeze microtoming and then preparing an electron photomicrograph of 3000 to 15000 x magnification. By measuring the diameter/thickness of a representative sample of at least 25 and preferably 50 filler particles one can obtain a relatively accurate value for the diameter/thickness ratio. The percentage of the filler below 40 micrometer (μm) diameter can be measured by screen analysis using a 325 mesh screen. Alternatively filler average particle size and percentages of filler below 40 and 20 μm can be determined by use of sedimentation analysis techniques, see Transactions of ASAE, p. 491 (1983).

Preferred compositions according to the invention are those containing from 5 to 15, more preferably from 6 to 12 percent of one or more inorganic fillers. In the more preferable fillers at least 99 percent by weight of the filler has an average particle diameter less than 20 μm . Highly preferred are those compositions incorporating fillers having an average diameter/thickness ratio (D/T) as measured according to the foregoing technique of from 6 to 18. Preferred fillers are uncalcined talcs and clays having very low free metal oxide content.

Preferred compositions according to the present invention comprise 55 to 75 percent by weight aromatic polycarbonate and 10 to 40 percent by weight of rubber modified homopolymer or copolymer and possess a dart impact at -29°C (-20°F) of at least 22.6 joules (200 in-lbs), a CLTE of less than $6.7 \times 10^{-5}/^{\circ}\text{C}$ ($3.7 \times 10^{-5}/^{\circ}\text{F}$) and a DTUL of at least 121°C (250°F).

The compositions are prepared by blending the foregoing components A, B and C. Desirably the components may be first mixed or dry blended prior to melt blending in an appropriate extruder or other melt blending device. The components may be combined and blended in any order. In addition to the

foregoing components, additional additives such as coupling agents, for example the polyfunctional organosilicon compounds disclosed in U.S. Patent No. 4,528,303 may be included in the blend. Pigments, antioxidants, processing aids, flame retardants, lubricants, mold release agents, and other additives may also be included in the composition.

5 Generally the addition of increased amounts of polycarbonate results in a final composition having improved DTUL. However, use of an excessive amount of polycarbonate results in reduction of dart impact strength. Injection molded components prepared from the resin blends of the present invention generally have an exceptionally smooth, defect free surface finish and are found to be less notch sensitive in impact resistance tests. In addition the compositions show improved resistance to hydrocarbon solvents such as
10 gasoline compared to polycarbonate resins.

In addition to the foregoing components, the polymeric blends may be further compounded with additional amorphous polymers. Examples of additional polymeric components with which the present composition may be further blended include the thermoplastic polyurethanes, amorphous polyesters, and polyarylate resins.

15 Having described the invention the following experiments are provided as further illustrative and are not to be construed as limiting. Parts and percentages are based on weight.

Experiment 1 Runs 1-4 and Comparative a

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A polycarbonate/ABS blend containing 64 weight percent bisphenol A polycarbonate, 36 weight percent of a mass polymerized polybutadiene modified ABS resin containing 20 percent rubber, 23 percent acrylonitrile and 57 percent styrene was dried for 4 hours at 99° C (210° F) in a circulated air dryer and then mixed in a polyethylene bag with 0.1 percent epoxidized soybean oil, 0.1 percent trisnonyl phenyl
25 phosphite (TNPP) and various amounts of an uncalcined clay (Tex 10R, available from Anglo-American Clay Company). The mixtures were then extruded through a Warner Pfleiderer ZSK-30 twin screw extruder. The heaters were maintained at 270° C (518° F), the screw was run at 400 RPM, and the throughput rate was about 13.6 Kg/hr (30 lbs/hour). Strands were cooled in a water bath and chopped. The granules were then
30 dried for 4 hours at 99° C (210° F) in a circulated air oven and molded into test specimens in an Arburg 28 ton injection molding machine at 288° C (550° F) melt temperature and 82° C (180° F) mold temperature. The physical properties of the resulting injection molded samples were then measured. In the resulting blend, greater than 99.99 percent of the particles had a diameter less than 44 Km. The average particle diameter/thickness was 14.3. Test results are contained in Table 1.

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Table 1

Run	Polycarbonate (%)	ABS (%)	Filler (%)	DTUL (° C)	CLTE x 10 ⁻⁵ /		Dart Impact -29° C	
					° C	(° F)	Joules	(in lbs)
1	64	32	4	--	6.86	(3.81)	54.7	(484)
2	63	31	6	--	6.17	(3.43)	41.8	(370)
3	61.6	30.4	8	--	6.32	(3.51)	35.5	(314)
4	60.3	29.7	10	128	6.19	(3.44)	39.6	(350)
a	67	33	0	--	7.56	(4.20)	59.7	(528)

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Experiment 2 Run 5 and Comparative b

55 The polycarbonate/ABS blend employed in Experiment 1 was blended with 6 percent each of two clay samples having diameter/thickness ratios shown in Table 2. These formulations were also molded substantially according to the technique of Experiment 1. The results of testing are shown in Table 2. The composition incorporating a clay having average particle diameter/thickness ratio of 16.3 had CLTE of 6.6 x 10⁻⁵/° C (3.65 x 10⁻⁵/° F) compared to 7.8 x 10⁻⁵/° C (4.28 x 10⁻⁵/° F) for compositions incorporating the

clay having diameter/thickness ratio of 2.8. All samples have the desired DTUL and dart impact values at -29° C (-20° F).

The diameter (or longest dimension) of the fillers as well as their thickness (shortest dimension of the 2 dimensions measurable) were measured from transmission electron photomicrographs (7500x) of micro-tome slices of the injection molded samples that had been exposed to accentuate the filler phase. The diameters and thicknesses of the fillers were measured manually with sample sizes of from twenty to fifty particles.

Table 2

Run	Polycarbonate (%)	ABS (%)	Clay (%)	D/T	CLTE x 10 ⁻⁵ /		% < 44 μ m
					° C	(° F)	
5	59	35	6	16.3 ¹	6.6	(3.65 ³)	99.99
b	59	35	6	2.8 ²	7.8	(4.28)	99.98

1 XF-3600 available from Anglo American Clay Co.

2 Translink 555 available from Englehard Ind.

3 Average of two samples.

Experiment 3 Runs 5-13

A polycarbonate/ABS blend was blended in a similar fashion as in Experiment 1 with a number of types of talc all having >99.99 percent of particles less than 44 μ m. The results of testing of these samples are shown in Table 3. It is seen that all samples containing 6 to 10 percent talc have the desired values of CLTE and dart impact at -29° C (-20° F).

Table 3

Run	Polycarbonate (%)	ABS (%)	Filler (%)	D/T	DTUL (° C)	CLTE x 10 ⁻⁵ /		Dart Impact -29° C	
						° C	(° F)	Joules	(in lbs)
5	63	31	6 ¹	9.0	--	6.96	(3.83)	60.3	(534)
6	63	31	6 ²	13.8	--	6.67	(3.67)	46.7	(413)
7	63	31	6 ³	12.3	--	7.02	(3.86)	58.1	(514)
8	61.6	30.4	8 ¹	9.0	--	6.44	(3.54)	52.1	(461)
9	61.6	30.4	8 ²	13.8	--	6.18	(3.40)	47.8	(423)
10	61.6	30.4	8 ³	12.3	125	6.64	(3.65)	41.2	(365)
11	60.3	29.7	10 ¹	9.0	--	6.11	(3.36)	54.8	(485)
12	60.3	29.7	10 ²	13.8	--	6.11	(3.36)	40.9	(362)
13	60.3	29.7	10 ³	12.3	--	5.64	(3.10)	52.4	(464)

1 MP10-52 available from Pfizer, D/T = 9.0, 99.99 percent of particles less than 20 μ m.

2 MP12-50 available from Pfizer, D/T = 13.8, 99.0 percent of particles less than 20 μ m.

3 MP25-38 available from Pfizer, D/T = 9.5, 99.5 percent of particles less than 20 μ m.

Experiment 4 Runs 14, 15 and Comparatives c and d.

The blend of polycarbonate and ABS resins from Experiment 1 was blended with 4 different talcs in amounts from 6 to 10 percent. Dart impact tests and CLTE were conducted on 12.5 x 12.5 cm (5 inch x 5 inch) plaques of the resulting blends and the unmodified polycarbonate/ABS blend. The 4 fillers were MP50-26 (D/T = 6.2, 98 percent <44 μm , 83 percent <20 μm , I_1) run 14; MP25-38 (D/T = 9.5, 99.99 percent <44 μm , 99.5 percent <20 μm , I_2) run 15; MP99-10 (D/T = 5.7, 77 percent <44 μm , 58 percent <20 μm , I_3) comparative c; and MP99-54 (D/T = 1.8, 98.0 percent <44 μm , 67 percent <20 μm , I_4) comparative d. All talcs were obtained from Pfizer. DTUL value for all samples was 124° C (255° F). The CLTE and dart impact resistance -29° C (-20° F) are contained in Figures 1 and 2 respectively.

As may be seen by reference to Figures 1 and 2, increasing percentages of filler result in products shaving reduced CLTE, however, dart impact strength is also reduced. Certain fillers cannot satisfy the simultaneous requirements of CLTE of less than 3.9 and dart impact -29° C (-20° F) of at least 11.3 joules (100 in-lbs).

Experiment 5 Runs 16-22, Comparison e

An N-phenylmaleimide modified ABS resin, and an emulsion ABS resin were blended with polycarbonate. The N-phenylmaleimide modified ABS had a composition of 19 percent AN, 6.5 percent butadiene, 63 percent styrene, and 11.5 percent N-phenylmaleimide and was prepared by solution polymerization of the monomers in the presence of dissolved polybutadiene rubber. This ABS was then compounded with 20 percent of an emulsion ABS containing 50 percent polybutadiene rubber grafted with 50/50 styrene/acrylonitrile copolymer. The polycarbonate was a bisphenol A polycarbonate, having a melt flow rate of 10 (CALIBRETM 300-10 available from The Dow Chemical Company).

Various clay and talc fillers are incorporated into the polymer in amounts from 4 to 10 percent by weight. Results are contained in Table 4.

Table 4

Run	Polycarbonate (%)	ABS (%)	Filler (%)	DTUL (° C)	Dart Impact -29° C		CLTE x 10 ⁻⁵ /	
					Joules	(in lbs)	° C	° F
16	61.75	33.25	4 ²	--	74.2	(657)	6.94	(3.82)
17	61	33	6 ¹	133	41.8	(370)	6.29	(3.43)
18	61	33	6 ²	--	61.5	(544)	6.87	(3.78)
19	61	33	6 ³	132	50.3	(445)	6.29	(3.46)
20	59.8	32.2	8 ¹	--	35.5	(314)	6.38	(3.51)
21	59.8	32.2	8 ³	--	30.5	(270)	5.64	(3.10)
22	58.5	31.5	10 ¹	--	41.4	(366)	5.91	(3.25)
e	65	35	0	--	62.0	(549)	7.22	(3.97)

1 Tex 10R clay available from Anglo American Clay Co. D/T = 14.3, 99.99 percent of particles have diameter <44 μm .

2 XF 3600 clay available from Anglo American Clay Co., D/T = 16.3, 99.99 percent <44 μm .

3 MP10-52 talc available from Pfizer, D/T = 9.0, 99.99 percent <44 μm .

Claims

1. A filled polymeric blend comprising:

(A) from 40 to 80 percent by weight of an aromatic polycarbonate;

(B) from 5 to 50 percent by weight of a rubber modified homopolymer or copolymer of a vinyl aromatic monomer;

(C) from 4 to 18 weight percent of an inorganic filler selected such that (i) at least 98 weight percent of the filler particles in the final blend have a particle diameter less than 44 μm and (ii) the average filler

particle diameter to thickness ratio is from 4 to 24,

said blend having a coefficient of linear thermal expansion (CLTE) of $3.9 \times 10^{-5}/^{\circ}\text{F}$ ($7.0 \times 10^{-5}/^{\circ}\text{C}$) or less, a dart impact at -29°C (-20°F) of at least 11.3 joules (100 in lb), and a heat distortion temperature under load (DTUL) per ASTM D-648-82 at 66 psi (455 kPa) of at least 110°C (230°F).

5 2. A polymeric blend according to Claim 1 having a CLTE of $6.7 \times 10^{-5}/^{\circ}\text{C}$ ($3.7 \times 10^{-5}/^{\circ}\text{F}$) or less.

3. A polymeric blend according to Claim 1 having a dart impact at -29°C (-20°F) of at least 22.6 joules (200 in lbs).

4. A polymeric blend according to Claim 1 comprising from 50 to 80 percent by weight of aromatic polycarbonate and from 5 to 46 percent by weight rubber modified homopolymer or copolymer.

10 5. A polymeric blend according to Claim 1 wherein at least 99 percent of the filler particles have a particle diameter less than $20\text{ }\mu\text{m}$.

6. A polymeric blend according to Claim 1 wherein the filler has an average diameter/thickness ratio of from 6 to 18.

15 7. A polymeric blend according to Claim 1 wherein the filler is selected from the group consisting of talc and uncalcined clay.

8. A polymeric blend according to Claim 1 wherein the rubber modified copolymer comprises a copolymer of styrene and acrylonitrile and optionally N-phenylmaleimide and the rubber is a homopolymer or copolymer of butadiene or an interpolymer of ethylene, propylene and a nonconjugated diene.

20 9. A fabricated article comprising a polymeric blend according to Claim 1.

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FIG. 1

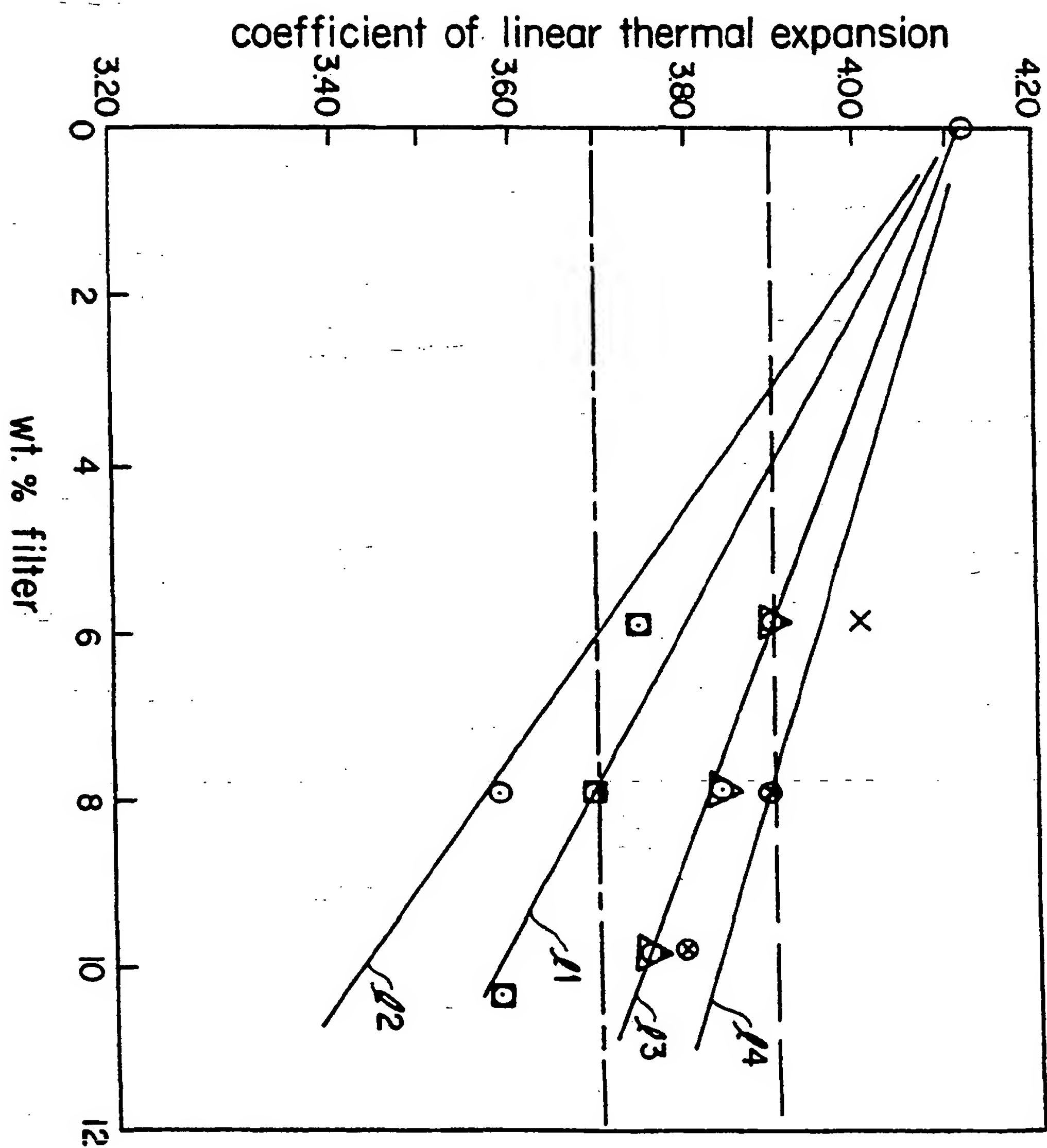
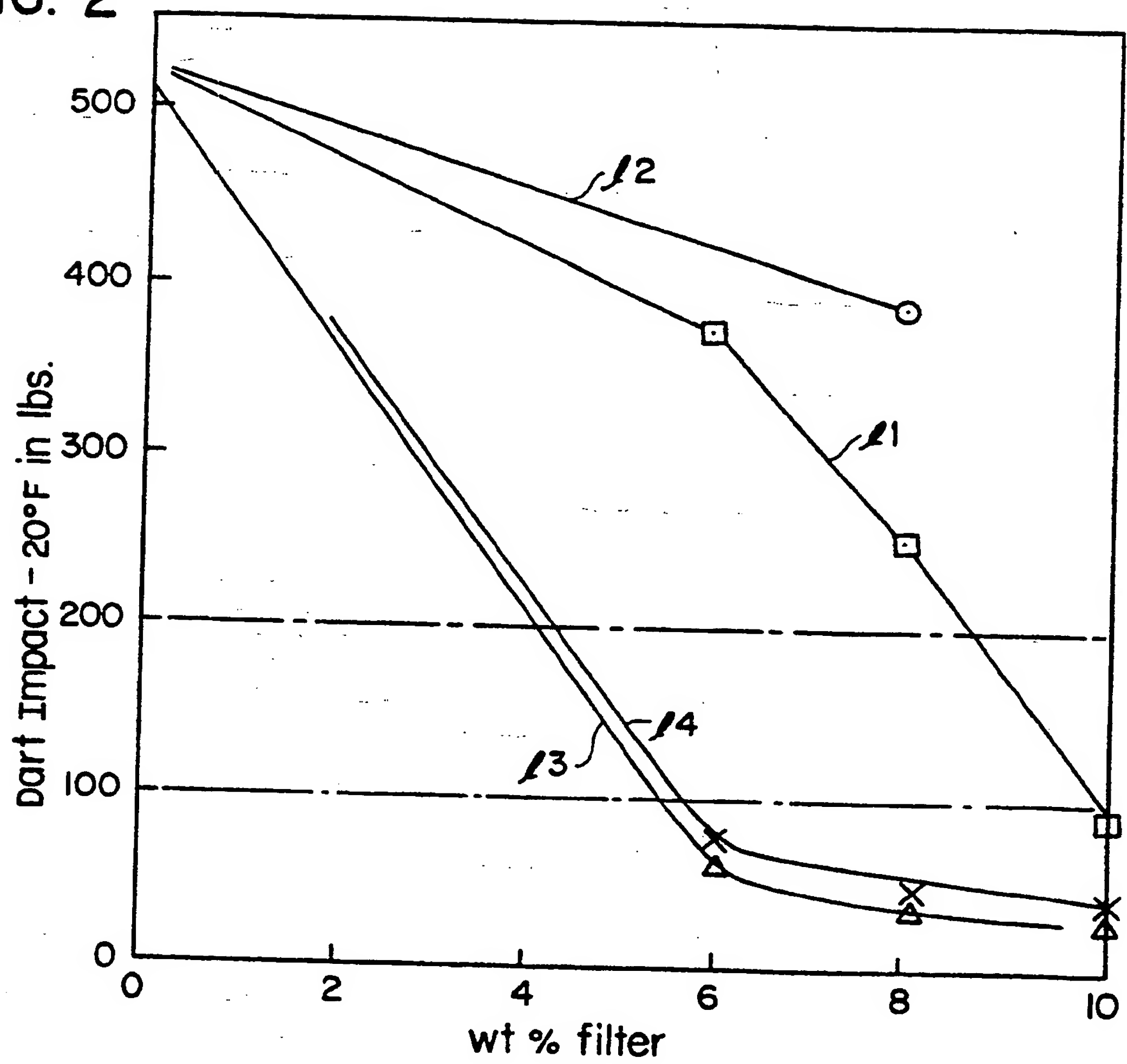


FIG. 2



(19)



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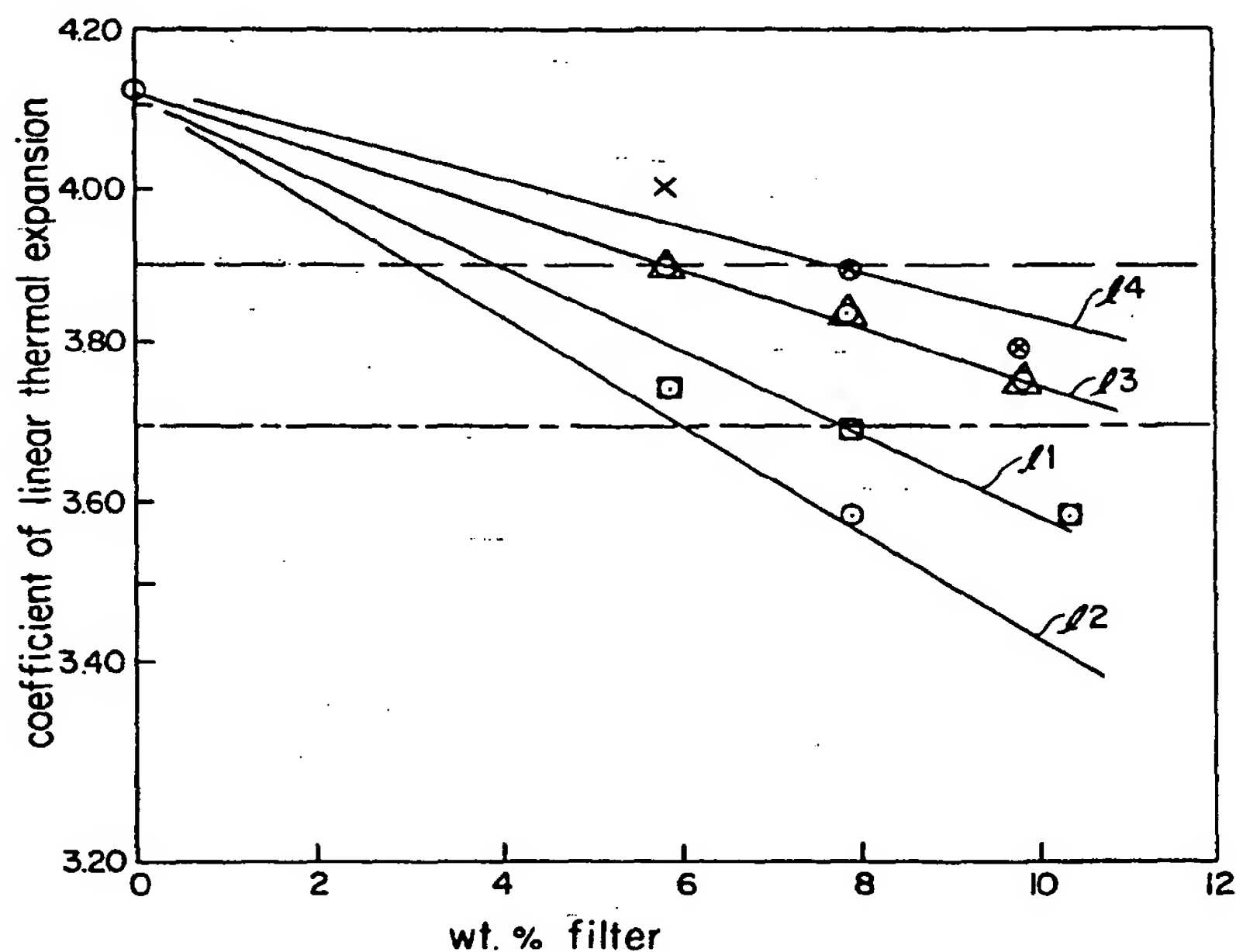
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26.02.92 Bulletin 92/09(71) Applicant: **THE DOW CHEMICAL COMPANY**
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FIG. 1



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EUROPEAN SEARCH REPORT

Application Number

EP 90 10 6536

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-2 534 265 (SUMITOMO NAUGATUCK CO LTD) * claims; page 6, lines 25-34; examples *	1	C 08 L 69/00 C 08 L 55/02 C 08 K 3/34 //
A,D	PATENT ABSTRACTS OF JAPAN vol. 1, no. 102 (C-025), 10 September 1977; & JP - A - 52063954 (SUMITOMO NAUGATUCK CO LTD) 26.05.1977 * abstract *	1,7	(C 08 L 69/00 C 08 L 55:02)
A,D	US-A-4 098 734 (Y.C. LEE) * claims 1-3,7 *	1,7	
A	EP-A-0 135 904 (MOBAY CHEMICAL CORP) * claims 1-4 *	1,7	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 L C 08 K
Place of search		Date of completion of search	Examiner
Berlin		19 November 91	VOIGTLAENDER R O J
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